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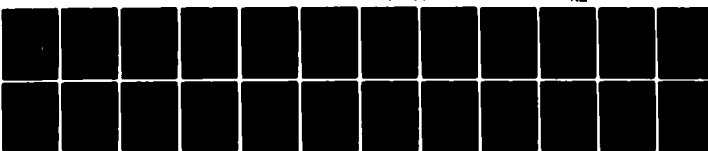
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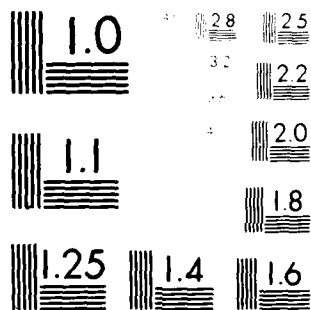
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XPS Study of Chemically Etched GaAs and InP

P. A. BERTRAND
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15 March 1982

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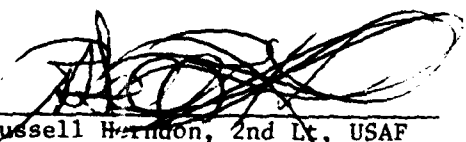
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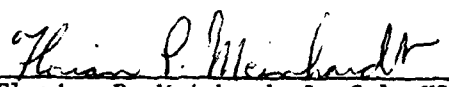
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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

The technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

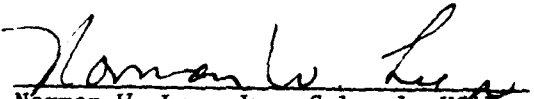


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The surface composition of p-type GaAs etched in HCl or Br ₂ in methanol, and n-type InP etched in HCl, H ₂ SO ₄ , HNO ₃ or Br ₂ in methanol have been studied by means of x-ray photoelectron spectroscopy (XPS). The surface compositions of GaAs and the binding energy of the surface As atoms vary with the etching solution and with the extent of oxidation of the surface. The full width at half-maximum of the Ga(3p) photoelectron peak increases upon exposure of etched GaAs to air. The XPS results are compared with Schottky barrier heights		

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previously measured for similarly prepared surfaces with Pb contacts. The amount of oxidized P on InP surfaces is higher after an HNO_3 etch than after HCl , H_2SO_4 , or Br_2 /methanol treatments. An HCl etch leaves an unoxidized slightly In-rich surface.

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PREFACE

It is a pleasure to acknowledge the assistance of J. L. Conner and L. U. Tolentino, who carried out some of the XPS experiments, and to thank Paul D. Fleischauer for many helpful discussions. This project was supported by the U.S. Air Force under Space Division contract F04701-81-C-0082.

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I. INTRODUCTION

Gallium arsenide and indium phosphide have many potential applications in semiconductor devices, such as microwave oscillators and high-frequency field-effect transistors. Understanding GaAs and InP surfaces is important to the development of these devices since the behavior of metal-semiconductor contacts depends directly on the properties of the semiconductor surface. In particular, the formation of Schottky barriers on GaAs is affected by the treatment of the material. Certain etching solutions result in higher Schottky barriers than others.¹

X-ray photoelectron spectroscopy (XPS) is an appropriate technique with which to study the surface chemistry of GaAs and InP. The binding energies of electrons photoejected from the inner electronic cores of atoms in the first few surface layers are measured. These binding energies depend on the atom involved in the photoejection and on the chemical state of the atom.² The relative amounts of the components of the surface layers can also be determined.

Experiments were performed to correlate surface properties of p-type GaAs with Schottky barrier heights. Samples etched in bromine (which produces a high barrier) and HCl (which produces a low barrier) were analyzed. The XPS results obtained are used to explain the observed difference in Schottky barriers. Several types of pretreatments of InP were studied: etching in sulfuric acid, nitric acid, hydrochloric acid, or a bromine in methanol solution, or oxidation. These treatments are being explored as possibilities for use in diode preparation.

¹M. McColl, M. F. Bottjer, A. B. Chase, R. J. Pederson, A. H. Silver, and J. R. R. Tucker, IEEE Trans MAG 15, 468 (1979).

²K. Siegbahn, et al., ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, (Almqvist and Wiksell, Upsalla, Sweden, 1967).

II. EXPERIMENTAL

The spectra were taken on a GCA/McPherson ESCA-36 x-ray photoelectron spectrometer equipped with an electrostatic analyzer. Control, data acquisition, and readout were all directed by a PDP-8E computer with a 24,000 word memory.

The samples of GaAs were polished (100) faces of p-type material, zinc-doped to a carrier concentration of $4.5 \times 10^{18} \text{ cm}^{-3}$. Sample G-1 was studied with no pretreatment. One of three etching solutions was used on each of the other samples. Samples G-2 and G-3 were etched for 15 min in concentrated HCl, followed by an ethanol rinse. Samples G-4 and G-5 were soaked in a 2% solution of Br_2 in methanol for 15 sec, followed by a methanol rinse. Sample G-6 was treated in two steps: a bromine etch for 15 sec, then a 1 min soak in concentrated HBF_4 . It was rinsed in methanol after etching. After analysis of the etched surfaces, samples G-2 and G-4 were exposed to air for 10 min and 5 min, respectively, and then reanalyzed.

The coupons of InP were polished (100) faces of n-type tin-doped InP with a carrier concentration of $3 \times 10^{17} \text{ cm}^{-3}$. Samples I-1 and I-2 were immersed in concentrated sulfuric acid for 5 min, whereas 9M H_2SO_4 was used to etch samples I-3 and I-4. Samples I-5 and I-6 were etched for 5 min with concentrated nitric acid, and samples I-7 and I-8 were etched for 3 min with concentrated hydrochloric acid. Samples I-9 and I-10 were etched for 15 sec in 2% Br_2 in methanol. These samples were all rinsed in methanol after etching. Sample I-11 was etched in Br_2 in methanol and was permitted to oxidize in air at room temperature for 2 h. Sample I-12 was oxidized for 10 min in O_2 at 400°C , while I-13 was oxidized for 2 h in air at 300°C .

The coupons were kept under methanol until they were placed in the vacuum chamber of the spectrometer. In this way, unintentional oxidation of the surfaces was minimized. Once the samples were loaded into the spectrometer, the vacuum chamber was quickly evacuated to a pressure of 10^{-6} Torr in less than 10 min. The spectra were taken at pressures of about 10^{-7} Torr.

In addition, samples of As, In and Ga metals, as well as As_2O_5 , As_2O_3 , Ga_2O_3 , In_2O_3 , K_2HPO_4 , $(\text{NaPO}_3)_3$, $\text{Na}_4\text{P}_2\text{O}_7$, and P_4O_{10} were observed for comparison purposes. The oxides and phosphates were obtained as reagent grade powders and were mounted by pressing into doublesided masking tape on Al coupons. The metals were observed after Ar ion sputtering to remove the surface oxides.

All binding energies are corrected to a carbon 1s binding energy of 285.0 eV to compensate for the effects of sample charging. The precision with which binding energy can be determined is ± 0.2 eV. The relative abundance ratios reported are determined from the intensity of the specified XPS peak, corrected for the tabulated differences in sensitivity of the spectrometer for the various elements. Intensities can be measured with a precision of 10 to 20%. The variation of intensity with depth into the material can be expressed as

$$\frac{I}{I_0} = 1 - e^{-D/\lambda \sin \theta} \quad (1)$$

where θ is the angle the x-rays make with the surface, λ is the electron mean free path, D is the depth, and I/I_0 is the fraction of the signal intensity originating above the depth D .

III. RESULTS

The XPS binding energies for the standard samples of Ga, As, In, As_2O_5 , As_2O_3 , Ga_2O_3 , In_2O_3 , K_2HPO_4 , $(\text{NaPO}_3)_3$, $\text{Na}_4\text{P}_2\text{O}_7$, and P_4O_{10} are listed in Table 1. Also listed are several literature values of the binding energies for these compounds. Agreement between measured and literature values is fair.

In Table 2 are listed the binding energies and relative abundance ratios of the As(3d) and Ga(3p_{3/2}) peaks of the GaAs coupons. The binding energy of the Ga is identical for all etched samples ($105.0 \text{ eV} \pm 0.2 \text{ eV}$), 1.3 eV higher than that of Ga metal (103.7 eV). The literature value is approximately 105 eV for GaAs surfaces cleaved in air or vacuum, or cleaned by Ar ion sputtering.^{3,4} The three oxidized samples have a higher Ga(3p_{3/2}) binding energy (105.7 eV) close to that of Ga_2O_3 (105.9 eV).

The As(3d) binding energies of the Br_2 -etched coupons and the HCl-etched coupons are not the same. The Br_2 -etched coupons have an As(3d) binding energy of 41.6 eV, which is 0.2 eV lower than that of As metal as measured in these experiments. On the other hand, the As (3d) binding energy of the HCl-etched coupons is 42.0 eV. This higher binding energy indicates a relative electron deficiency on the As atoms of the HCl-etched samples compared to the Br_2 -etched samples.

After air exposure, the surfaces of G-2 and G-4 have oxidized (Figs. 1 and 2). In both cases, the Ga(3p) peak has broadened and shifted to higher binding energy, as mentioned previously. A second As(3d) peak, with a binding energy of 45.0 eV, has appeared on sample G-2. This peak corresponds to oxidized As, while the lower binding energy peak is attributed to GaAs. For sample G-4, which had previously been etched in HCl, there is a broadening and

³Y. Mizokawa, H. Iwasaki, R. Nishitani, and S. Nakamura, J. Electron Spectrosc. Relat. Phenom. 14, 129 (1978).

⁴T. Lane, C. J. Veseley, and D. W. Langer, Phys. Rev. B 6, 3770 (1972).

Table 1. XPS Binding Energies of Standard Compounds

<u>Material</u>	<u>Ga(3p_{3/2}), eV</u>	<u>As(3d), eV</u>	<u>In(3d_{3/2}), eV</u>	<u>In(M₄N₄₅N₄₅), eV</u>	<u>P(2p), eV</u>	<u>Ref.</u>
Ga (sputtered)	103.7					a
Ga ₂ O ₃	105.9					a
		105.7				b
As (sputtered)		41.8				a
			42.1			c
			41.6			d
As ₂ O ₃		45.6				a
			45.2			b
			46.0			c
			45.3			d
			45.6			e
As ₂ O ₅		46.5				a
			46.4			c
			46.3			d
			47.0			e
			46.0			f
In (sputtered)			443.8	409.4		a
In ₂ O ₃			444.6	406.2		a
				444.7	406.2	g
K ₂ HPO ₄					133.0	a
					132.4	h
(NaPO ₃) ₃					133.8	a
					134.1	h
Na ₄ P ₂ O ₇					133.5	a
P ₄) ₁₀					135.7	a
					135.4	i

a This work

b G. E. McGuire, G. K. Schweitzer, and T. A. Carlson, *Inorg. Chem.* **12**, 2450 (1973).

c W. J. Stec, W. E. Morgan, R. G. Albridge, and J. R. van Waser, *Inorg. Chem.* **11**, 219 (1972).

d Y. Mizokawa, H. Iwasaki, R. Nishitani, and S. Nakamura, *J. Elec. Spectrosc. Relat. Phenom.* **14**, 129 (1978).

e C. W. Wilmsen and R. W. Kee, *J. Vac. Sci. Technol.* **15**, 1514 (1978).

f L. D. Hulet and T. A. Carlson, *Appl. Spec.* **25**, 33 (1971).

g A. W. C. Lin, N. R. Armstrong, and T. Kuwana, *Anal. Chem.* **49**, 1228 (1977).

h M. Pelavin, P. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.* **74**, 1116 (1970).

i C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979).

Table 2. Observed XPS Binding Energies and Relative Abundance Ratios for GaAs.

<u>Sample Number</u>	<u>Sample Treatment</u>	<u>Ga(3p_{3/2}), eV</u>	<u>As(3d), eV</u>	<u>Ca/As^a</u>
G-1	Unetched	105.8, broad	41.7 45.1	1.45
G-2	HCl etch	105.1	42.0	0.76
G-3	HCl etch	105.1	42.0	0.90
G-4	Br ₂ etch	105.0	41.6	0.99
G-5	Br ₂ etch	105.0	41.7	0.95
G-6	Br ₂ /HBF ₄	105.0	41.7	0.88
G-2b	Br ₂ etch, oxidized	105.5, broad	41.4, broad	0.95
G-4b	HCl etch, oxidized	105.7, broad	41.3 45.0	1.55

^aRatios of peak areas, corrected as discussed in text.

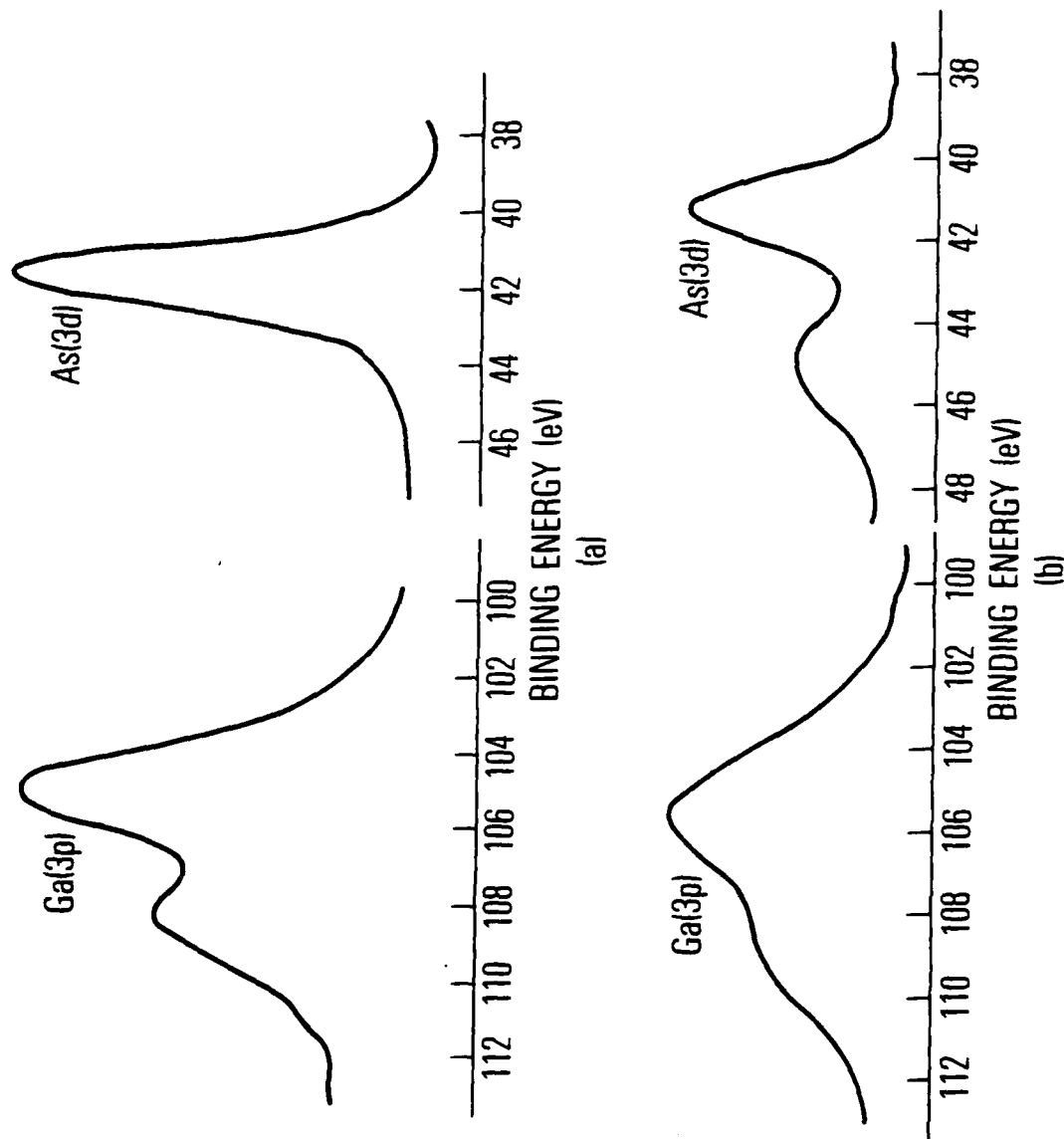


Fig. 1. X-ray Photoelectron Spectra of $\text{Br}_2/\text{CH}_3\text{OH}$ -etched GaAs. (a) Freshly Etched GaAs. (b) After 5 Minutes Air Exposure.

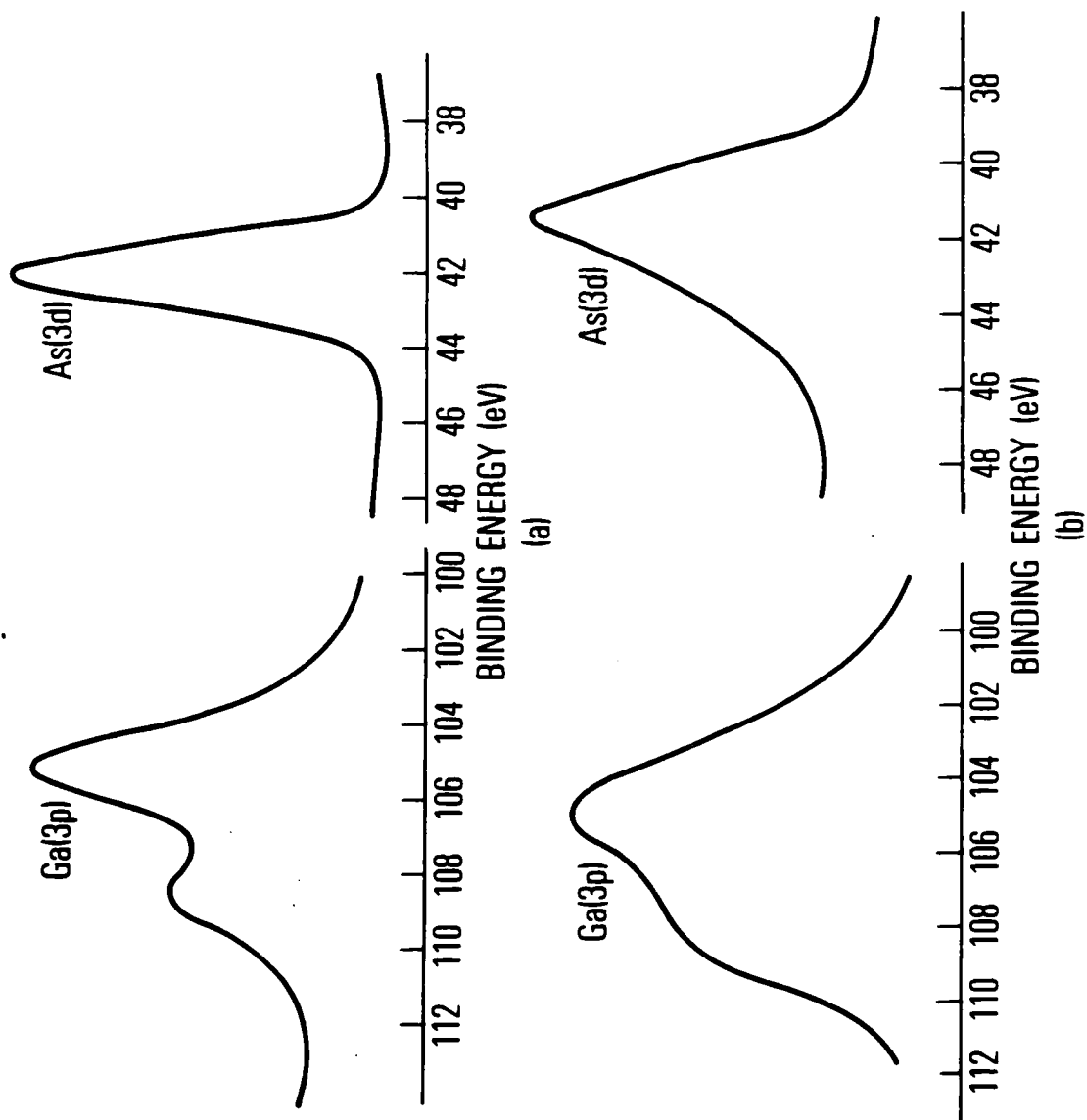


Fig. 2. X-ray Photoelectron Spectra of HCl-etched GaAs. (a) Freshly Etched GaAs. (b) After 5 Minutes Air Exposure.

shifting of the As(3d) peak. After air exposure, the binding energy is 41.4 eV, identical to that of G-2. The high binding energy tail that broadens the peak may be due to unresolved contributions from oxidized As.

The relative amounts of Ga and As on the surfaces of the coupons change with etching solution (Table 2). The Br₂ etch leaves the surface almost stoichiometric, whereas before etching the surface was rich in Ga. After only 5 min exposure of G-2 to air, Ga enrichment of the surface has occurred. Similarly, the Ga/As ratio of the HCl-etched coupon G-4 increased from 0.76 before oxidation to 0.95 after 10 min in air.

In Table 3 are presented the XPS binding energies for the InP coupons. An important observation can be made at once. The In (3d_{5/2}) binding energy is identical for all of the samples regardless of pretreatment, except for I-13. The M₄N₄₅N₄₅ Auger peak kinetic energy, 408.1 eV, is also constant. A characteristic of an atom that can be derived from XPS data is the "Auger parameter," which is the binding energy of the XPS peak minus the kinetic energy of the Auger peak. It is often a more sensitive indicator of a particular compound than the XPS binding energy and is unaffected by sample charging. For these InP coupons, the Auger parameter is 36.4 ± 0.3 eV. In this study, it has been measured as 38.4 eV for In₂O₃ and 34.9 eV for In. The constancy of the Auger parameter for InP in this work indicates that the chemical state of In is not changing measurably with pretreatment. A surface compound with an In oxidation state different from InP would be observable if it were present to an extent greater than one-fourth monolayer. Since only the InP form of In is observed, an upper limit is placed on the amount of other possible In compounds such as oxides present in the surface layers of all samples except I-13.

Sample I-13 was heavily oxidized in air. This is the only treatment of those described here in which two different chemical states of In can be observed. A peak with higher binding energy than InP (445.7 eV as compared to 444.5 eV) is also present, indicating a form of In that is more electron-deficient than InP. It is probably an oxidized form of In, but has a higher binding energy than that of In₂O₃ measured in these experiments (444.6 eV), possibly as a result of structural differences or the presence of hydroxyls.

Table 3. XPS Binding Energies and Auger Electron Kinetic Energies for InP

<u>Sample Number</u>	<u>Sample Treatment</u>	<u>In(3d_{5/2}), eV</u>	<u>In(M₄N₄S₄), eV</u>	<u>P(2p), eV</u>
I-1	Conc. H ₂ SO ₄ etch	444.7	407.9	129.3 133.7
I-2	Conc. H ₂ SO ₄ etch	444.7	408.4	129.3 133.7
I-3	9M H ₂ SO ₄ etch	444.6	408.6	129.2 133.5
I-4	9M H ₂ SO ₄ etch	444.3	408.6	129.1 133.6
I-5	HNO ₃ etch	444.6	408.3	129.0 133.5
I-6	HNO ₃ etch	444.5	408.3	129.0 133.3
I-7	HCl etch	444.8	407.8	129.6 133.7
I-8	HCl etch	444.9	408.0	129.6 133.6
I-9	Br ₂ etch	444.6	408.1	129.3 133.5
I-10	Br ₂ etch	444.3	408.5	129.0 133.5
I-11	Oxidized	444.4	408.1	129.0 133.7
I-12	Oxidized	444.5	407.5	129.2 133.8
I-13	Heavily oxidized	444.5, 445.7	405.0	129.0 134.0

Two chemical states of P are present on each sample (Figure 3). One state has a 2p binding energy of 129.1 eV, comparable to that of various phosphides (128.9 to 129.5 eV)⁵. The other measured binding energy (133.6 eV) is indicative of oxidized phosphorus, such as phosphates and phosphites by comparison both to the literature (133.0 to 134.0 eV)⁵ and to values measured in this study (Table 1). The phosphide state is identified as InP. The oxidized phosphorus is caused by surface oxidation, both intentional and unintentional, of the samples. It is generally denoted P_2O_5 in the literature, although comparison of the surface oxide binding energy (133.6 eV) with that of the P_4O_{10} standard (135.7 eV) clearly indicates that this identification is not accurate. (The proper chemical formula for this oxide is P_4O_{10} since it is a dimer.) The surface phosphorus oxide produced on initial oxidation of InP does not contain as electron-deficient a P as does P_4O_{10} . This may be due to the presence of P-In bonds as well as P-O bonds, in structures analogous to phosphonates.

The relative amounts of phosphide and oxidized P in the surface layers vary with pretreatment of the InP coupons (Table 4). Samples etched in concentrated H_2SO_4 , HCl, or Br_2 have very little oxidized phosphorus, whereas those etched in concentrated HNO_3 or intentionally oxidized in air have more. InP oxidizes readily in air, and the small amount of oxidized P on the H_2SO_4 and Br_2 treated samples is probably caused by unintentional oxidation of the coupon during loading into the spectrometer. Exposure of InP to concentrated nitric acid causes more oxidation than that experienced by the eight coupons just mentioned, as indicated by the oxidized phosphorus to phosphide ratio of 0.20. Even more oxidized P is formed by prolonged exposure to air; the oxidized phosphorus to phosphide ratio is 0.35 for samples I-11 and I-12. Using Eq. (1), with an electron escape depth $\lambda = 10\text{\AA}$, this represents a layer approximately 2 \AA thick, or an entire monolayer of oxidized P in the InP surface.

⁵C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, Handbook of X-ray Photoelectron Spectroscopy, (Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979).

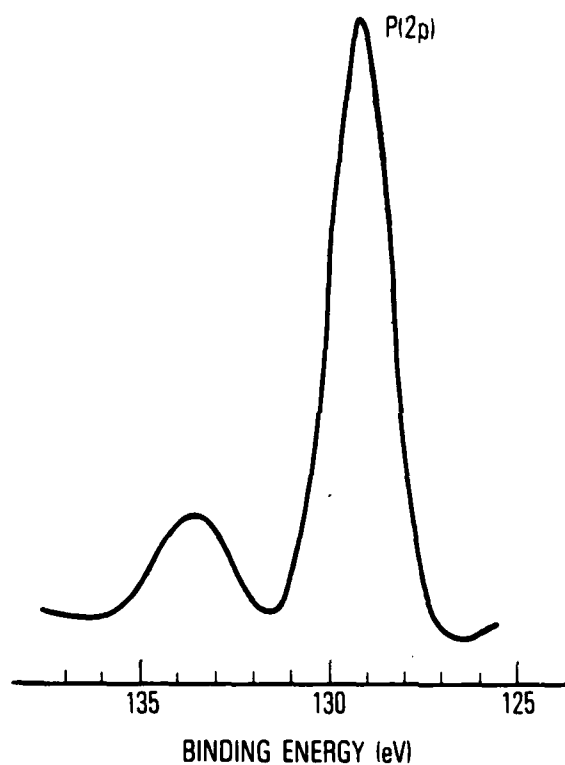


Fig. 3. X-ray Photoelectron Spectrum of Phosphorus for Sample I-5, InP Etched with HNO_3 .

Also listed in Table 4 are the ratio of In to phosphide and the ratio of total In to total phosphorus (phosphide plus oxidized P) for the InP samples. On the average, the surface is stoichiometric in In and P. There are small differences between the samples, but the magnitude of these variations is comparable to the experimental error. However, sample I-8 (after an HCl etch) has much more In than P on the surface; the reason for the difference in In to P ratio between samples I-7 and I-8 is not clearly understood at the present time.

Table 4. XPS Relative Abundance Ratios for InP

<u>Sample Number</u>	<u>Sample Treatment</u>	<u>In/P(129 eV)</u>	<u>In/P (Total)</u>	<u>P(133 eV)/P(129 eV)</u>
I-1	Conc. H ₂ SO ₄ etch	0.88	0.81	0.08
I-2	Conc. H ₂ SO ₄ etch	1.0	1.0	0.07
I-3	9M H ₂ SO ₄ etch	1.1	1.0	0.07
I-4	9M H ₂ SO ₄ etch	1.0	0.98	0.06
I-5	HNO ₃ etch	0.90	0.76	0.18
I-6	HNO ₃ etch	1.1	0.94	0.21
I-7	HCl etch	1.2	1.1	0.11
I-8	HCl etch	2.0	1.9	0.03
I-9	Br ₂ etch	1.1	1.1	0.06
I-10	Br ₂ etch	1.0	0.93	0.08
I-11	Oxidized	1.1	0.79	0.39
I-12	Oxidized	1.2	0.91	0.30
I-13	Heavily oxidized	0.91, 0.72	0.92	0.77

IV. DISCUSSION

The XPS results for GaAs presented in this report have a direct bearing on the measured Schottky barriers for identically prepared samples. After a Br_2 etch, the barrier is 0.65 V, whereas after an HCl etch, the barrier is 0.4 V. After air exposure, both surfaces have the same Schottky barrier, 0.65 V.¹ The XPS results exactly parallel the Schottky barrier measurements. After an HCl etch, the binding energy of the As atoms increases, relative to a Br_2 etched surface, and the surface becomes slightly As-rich. After air exposure, the As atoms return to the same binding energy as that of the Br_2 etched samples, and the surface becomes richer in Ga.

From the results of photoemission experiments,^{6,7} it has been shown that the surface states of the (110) surface of GaAs comprise two bands, an As-derived band within the valence band near the valence band maximum and a Ga-derived band in the conduction band. The As-derived band is filled; the As atoms have dangling bonds. The electrons of the surface Ga atoms are involved in backbonding to inner layers, and the Ga-derived states in the conduction band are empty.^{7,8} The photoemission spectra of the (100) surface are similar to those of the (110) surface; there are no empty surface states in the band gap.⁹ The Ga and As surface atoms have different hybridizations on the (100) surface than on the (110) surface,¹⁰ but the surface state levels still fall within the bulk valence and conduction bands. For a p-type semiconductor, the Schottky barrier is determined by the difference in energy between the Fermi

⁶J. L. Freeouf and D. E. Eastman, Crit. Rev. Solid State Sci. 5, 245 (1975).

⁷P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, Appl. Phys. Lett. 25, 511 (1974).

⁸C. C. Chang, P. H. Citrin, and B. Schwartz, J. Vac. Sci. Technol. 14, 943 (1977).

⁹J. Massies, P. Devoldere, and N. T. Linh, J. Vac. Sci. Technol. 15, 1353 (1978); R. Ludeke and L. Ley, J. Vac. Sci. Technol. 16, 1300 (1979).

¹⁰W. A. Harrison, J. Vac. Sci. Technol. 16, 1492 (1979).

level of the contacting metal-semiconductor system and the valence band maximum at the semiconductor surface.

The defect model of Schottky barrier formation states that the surface Fermi level of the semiconductor can be changed by the presence of defects at or near the semiconductor surface, and that it can be pinned at the new position.¹¹ Energies of some possible defects have been calculated for GaAs: an anion vacancy (an acceptor defect) has an energy of 0.65 eV below the conduction band minimum, whereas a cation vacancy (a donor defect) has an energy of 0.8 eV below the conduction band minimum.¹²

The Schottky barrier measurements for p-type GaAs can be understood by the defect model and the XPS results presented here. An HCl etch produces an As-rich surface, which has many donor defects. These defects could be cation vacancies, anions in cation positions, or other more complex defects. The energy levels of these defects have not been calculated, except for the cation vacancy mentioned above, which has an energy level below the Fermi level of the perfect surface. If we take this defect as an example, the Fermi level of the HCl-etched As-rich surface could be pinned at a lower energy than that of a Br₂-etched, stoichiometric surface. The difference between the Fermi level and the valence band maximum has thus decreased. The Schottky barrier should be lower for the HCl-etched surface than for the Br₂-etched surface, just what is observed experimentally.

In addition to the increased number of As atoms on an HCl-etched GaAs surface, the binding energy characteristic of these atoms is unlike that of As atoms on a stoichiometric GaAs surface. This is probably caused by an increase in As-As bonding with respect to As-Ga bonding. As-Ga bonds are more ionic than As-As bonds. Arsenic atoms have a higher electronegativity than Ga

¹¹P. W. Chye, I. Lindau, P. Pianetta, C. M. Garner, C. Y. Su, and W. E. Spicer, *Phys. Rev. B* **18**, 5545 (1978).

¹²W. E. Spicer, I. Lindau, C. Y. Su, P. R. Skeath, and A. Landau, 7th Annual Conference on the Physics of Compound Semiconductor Interfaces, Paper No. 33, Estes Park, Colorado, January 29-31, 1980, Paper No. 33.

atoms (2.0 as compared to 1.6 on Pauling's scale) so the As atom in an As-Ga pair will have a higher electron density, and thus a lower XPS binding energy than in an As-As pair.

Oxidation also affects the surface Fermi level of GaAs. This is evidenced in the XPS results, which show binding energy and relative surface abundance changes upon oxidation, and in the Schottky barrier measurements. A detailed understanding of the oxidation process and its effects on the semiconductor donor and acceptor levels near the surface is not presently available. The chemistry of etched and oxidized surfaces is different, as indicated by the XPS results. However, the Schottky barrier heights suggest that the Fermi level of the oxidized surface is pinned near its position on the stoichiometric surface, since the barriers for Br₂-etched and oxidized GaAs are the same.

Schottky barrier measurements have not been made for InP prepared identically to the samples used in these experiments, so a detailed comparison of chemical and electronic measurements describing the metal-semiconductor interface is not possible for InP.

The etching solutions studied here appear mainly to regulate the amount of oxidized P on the InP surface. Sulfuric acid, hydrochloric acid, and bromine remove surface oxides, whereas nitric acid does not since it is itself a strong oxidizing agent. It has been reported that the amount of oxidized P at the interface affects the Schottky barrier height. When more oxide is present, the barrier is higher.¹³ Our results thus indicate that air-oxidized surfaces should have a higher Schottky barrier than nitric-acid-etched surfaces, which, in turn, should have a higher Schottky barrier than unoxidized surfaces.

An HCl etch changes the stoichiometry of the InP surface, as well as removing the surface oxides. Unlike the GaAs case, however, for InP the

¹³A Christou and W. T. Anderson, Jr., Solid-State Electron. 22, 857 (1979).

surface becomes cation rich, not anion rich. There is a vigorous chemical reaction with liberation of gas during the HCl etching of InP as the Cl^- ion interacts with and removes phosphorus from the surface.

The oxidation of III-V semiconductors begins with the adsorption of oxygen on the Group V atom, P in the case of InP.¹⁴ For GaAs, the initial adsorption of O on As causes an increase in the As(3d) XPS binding energy, but does not affect the Ga energy levels.¹⁴ Similarly, for InP, oxidized P is observed before any change in the In levels occurs. Further oxidation of GaAs proceeds rapidly. After 5 min of exposure to air a mixed oxide (Ga_2O_3 and As_2O_3) layer has formed. This step does not occur as rapidly for InP; the surface P oxidizes, but oxidation of In requires higher temperatures and longer times than Ga oxidation in GaAs, because of the difference in relative stabilities of the two oxides.

The XPS results presented here clearly indicate the necessity of considering the detailed chemistry of a compound semiconductor surface in order to predict the results of etching or other treatments. This same detailed chemistry can be used to gain insight into the electronic properties of such surfaces.

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